Table 3. *Comparison of the torsion angles (°) in the* As *heterocyclic ring and corresponding phosphorus analog*

|  | $X = $ As | $X = $ P |
|---|---|---|
| $X$–C(1)–C(2)–C(3) | −57·1 (11) | −58·0 (9) |
| C(2)–C(3)–C(4)–C(5) | −64·9 (16) | −64·0 (12) |
| C(1)–C(2)–C(3)–C(4) | 63·4 (14) | 63·0 (11) |
| C(5)–$X$–C(1)–C(2) | 49·1 (8) | 52·2 (7) |
| C(4)–C(5)–$X$–C(1) | −49·5 (9) | −52·9 (8) |
| C(3)–C(4)–C(5)–$X$ | 58·5 (13) | . 59·6 (10) |

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# Tetraphenylarsonium Tetra(selenocyanato)aurate(III)

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**Abstract.** [As(C₆H₅)₄][Au(SeCN)₄], $M_r = 1000·2$, monoclinic, $C2/c$, $a = 21·226$ (4), $b = 6·460$ (1), $c = 22·307$ (4) Å, $\beta = 99·42$ (2)°, $V = 3017$ Å³, $Z = 4$, $D_x = 2·20$ Mg m⁻³, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 10·7$ mm⁻¹, $F(000) = 1856$, $T = 293$ K. The structure was refined to $R = 0·046$ for 2431 absorption-corrected observed reflections. The anion is planar, with Au–Se 2·457, 2·467 (1) Å. The gold and arsenic atoms occupy special positions with crystallographic symmetry $\bar{1}$ and 2 respectively.

**Introduction.** Little is known about complexes of gold with selenium donor ligands. Crystal structure determinations have been performed only for chloro(triphenylphosphine selenide)gold(I) (Hussain, 1986), (Ph₃PAu)₃Se⁺PF₆⁻ (Lensch, Jones & Sheldrick, 1982) and the gold(II) ylide complex [{Au(CH₂)₂PPh₂}₂(Cl)(PhSe)] (Porter & Fackler, 1987). We have begun a study of gold–selenium complexes and report here the structure of Ph₄As⁺Au(SeCN)₄⁻. Details of the preparation will be published elsewhere.

**Experimental.** Wine-red plates were obtained by diffusion of petrol ether into a solution in dichloromethane. The crystals are air stable.

A crystal 0·4 × 0·35 × 0·05 mm [plate face (10Ī)] was used to collect 3112 profile-fitted intensities (Clegg, 1981) on a Stoe–Siemens four-circle diffractometer (monochromated Mo $K\alpha$ radiation, $2\theta_{max} = 53°$, quadrant $\pm h + k + l$). Three check reflections indicated crystal decay of *ca* 5% and the intensities were corrected accordingly. Absorption corrections based on $\psi$ scans were also applied; transmission factors were 0·22–1·00. Merging equivalents gave 3030 unique reflections ($R_{int} = 0·023$), of which 2431 with $F > 4\sigma(F)$ were used for all calculations (program *SHELX*76; Sheldrick, 1976). Index ranges: $|h| \le 26$, $k \le 7$, $l \le 28$. Cell constants were refined from $2\theta$ values of 62 reflections in the range 20–23°.

The structure was solved by the heavy-atom method and refined on $F$ to $R = 0·046$, $wR = 0·051$ |non-H atoms anisotropic, H atoms included using a riding model; full matrix, 175 parameters; weighting scheme

## Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($\text{Å}^2 \times 10^3$)

Equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|  | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Au | 7500 | 2500 | 5000 | 43 (1) |
| As | 5000 | 1926 (2) | 7500 | 32 (1) |
| Se(1) | 6943 (1) | 4085 (2) | 5772 (1) | 61 (1) |
| Se(2) | 8351 (1) | 5100 (1) | 5226 (1) | 64 (1) |
| C(1) | 7474 (4) | 6247 (16) | 6064 (4) | 67 (3) |
| N(1) | 7774 (4) | 7652 (12) | 6260 (5) | 90 (3) |
| C(2) | 8904 (4) | 4432 (14) | 4701 (3) | 60 (3) |
| N(2) | 9262 (4) | 4096 (15) | 4389 (3) | 79 (3) |
| C(11) | 4943 (3) | 3629 (11) | 6791 (3) | 36 (2) |
| C(12) | 4427 (4) | 3481 (12) | 6328 (3) | 50 (2) |
| C(13) | 4419 (4) | 4679 (15) | 5812 (3) | 62 (3) |
| C(14) | 4907 (4) | 6006 (13) | 5763 (3) | 61 (3) |
| C(15) | 5421 (4) | 6196 (13) | 6234 (3) | 54 (3) |
| C(16) | 5441 (3) | 4986 (11) | 6756 (3) | 45 (2) |
| C(21) | 5757 (3) | 232 (11) | 7559 (3) | 39 (2) |
| C(22) | 6152 (3) | 398 (13) | 7132 (3) | 50 (3) |
| C(23) | 6679 (4) | −763 (14) | 7183 (4) | 65 (3) |
| C(24) | 6824 (4) | −2129 (15) | 7662 (6) | 76 (4) |
| C(25) | 6442 (4) | −2325 (13) | 8072 (5) | 59 (3) |
| C(26) | 5885 (3) | −1133 (12) | 8039 (3) | 48 (2) |

## Table 2. *Selected bond lengths* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| Au—Se(1) | 2·467 (1) | Au—Se(2) | 2·457 (1) |
| As—C(11) | 1·914 (6) | As—C(21) | 1·931 (7) |
| Se(1)—C(1) | 1·845 (9) | Se(2)—C(2) | 1·841 (9) |
| C(1)—N(1) | 1·153 (12) | C(2)—N(2) | 1·131 (12) |

| | | | |
|---|---|---|---|
| Se(2)—Au—Se(1) | 89·6 (1) | C(21)—As—C(11) | 108·7 (3) |
| C(1)—Se(1)—Au | 103·0 (3) | C(2)—Se(2)—Au | 103·5 (3) |
| N(1)—C(1)—Se(1) | 175·8 (9) | N(2)—C(2)—Se(2) | 176·8 (8) |
| Se(1)—Au—Se(1$^{i}$) | 180·0 | Se(1)—Au—Se(2$^{i}$) | 90·4 (1) |
| C(11)—As—C(11$^{ii}$) | 109·9 (3) | C(11)—As—C(21$^{ii}$) | 109·3 (3) |

Symmetry operators: (i) $1·5 - x$, $0·5 - y$, $1 - z$; (ii) $1 - x$, $y$, $1·5 - z$.

$w^{-1} = \sigma^2(F) + 0·0005\ F^2$; extinction correction of the form $F_{corr} = F_c/(1 + xF_c^2/\sin 2\theta)^{0·25}$, where $x$ refined to $6·2\ (4) \times 10^{-7}$; max. $\Delta/\sigma = 0·003$; max. features in final $\Delta\rho$ map $+1$, $-1·5\ \text{e Å}^{-3}$]. Atomic scattering factors those of *SHELX*. Atomic coordinates are given in Table 1, selected bond lengths and angles in Table 2.*

**Discussion.** The Au atom occupies the symmetry centre $0·75$, $0·25$, $0·5$ and the coordination at Au is thus exactly planar; in fact all atoms of the anion lie in a plane (mean absolute deviation 0·007 Å). The seleno-cyanate ligands are bonded to gold through Se, as would be expected for a soft-metal centre. The Au—Se bond lengths are 2·457, 2·467 (1) Å; *cf.* 2·425–2·457 (2) Å in (Ph$_3$PAu)$_3$Se$^+$ [six independent bond lengths in two cations (Lensch *et al.*, 1982)], 2·371 (2) Å in (Ph$_3$PSe)AuCl (Hussain, 1986) and

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*\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a full list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44128 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.*
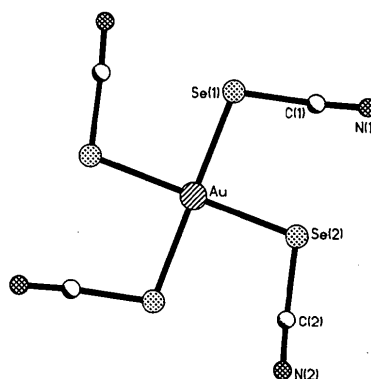


Fig. 1. The Au(SeCN)$_4^-$ anion in the crystal of the title compound. Radii are arbitrary.



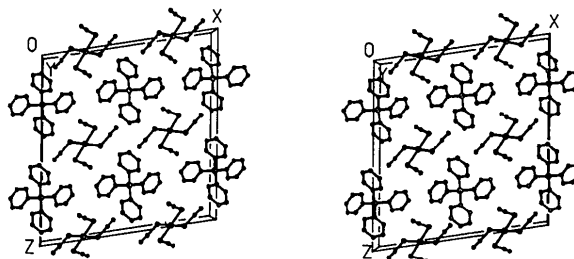Fig. 2. Stereographic packing diagram of the title compound, viewed along **y**. H atoms omitted for clarity.

2·469 (2) Å in the gold(II) ylide complex (Porter & Fackler, 1987). More data on Au—Se bond lengths are clearly needed before a useful comparison can be made. The anion is shown in Fig. 1; the angles at selenium (103°) lead to a swastika geometry.

The packing diagram (Fig. 2) shows that the cations and anions form separate columns parallel to the *b* axis. The structural relationships of Ph$_4$A$^+$ salts ($X$ = P, As) have been discussed by Müller (1980); preferred space groups are the tetrahedral $I\bar{4}$ and $P4/n$ [the latter was found for Ph$_4$As$^+$AuCl$_4^-$ (Jones, Guy & Sheldrick, 1975)] and space groups of lower symmetry derived by group/subgroup relationships. The pseudo-tetragonal nature of the current structure is apparent from Fig. 2 (the anions are inclined to the *xz* plane, however), but the *C2/c* structure type cannot be derived from the two ideal forms (Müller, 1980).

The cation displays the expected tetrahedral geometry, the arsenic atom lying on the twofold axis 0·5, *y*, 0·75.

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# Structure of the Beta Form of Bis(diethyldithiocarbamato)nickel(II)

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**Abstract.** [Ni($C_5H_{10}NS_2$)$_2$], $M_r = 355 \cdot 25$, tetragonal, $P4_2/n$ (No. 86), $a = 16 \cdot 244$ (3), $c = 6 \cdot 327$ (1) Å, $V = 1669 \cdot 4$ (7) Å$^3$, $Z = 4$, $D_x = 1 \cdot 41$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) $= 0 \cdot 71073$ Å, $\mu = 16 \cdot 32$ cm$^{-1}$, $F(000) = 743 \cdot 87$, $T = 298$ K. Convergence to final conventional $R$ values of $R = 0 \cdot 0321$ and $wR = 0 \cdot 0370$ was obtained using 79 variable parameters and 1105 reflections with $|F_o|^2 > 3\sigma(|F_o|^2)$. The unit cell consists of four discrete bis(diethyldithiocarbamato)Ni$^{II}$ molecules. Each four-coordinate square-planar Ni$^{II}$ center is bonded to four S atoms of two chelating diethyldithiocarbamate ligands. The Ni, two N and four S atoms of each discrete unit lie in the same plane. The Ni–S distances are 2·204 (1) and 2·192 (1) Å, the C–S distances are 1·711 (3) and 1·725 (3) Å.

**Introduction.** The diethyldithiocarbamate ligand, [$S_2CN(C_2H_5)_2$]$^-$ (dtc), gives metal complexes with a wide variety of transition metals. Our continued interest (Fackler, Niera, Campana & Trzcinska-Bancroft, 1984) in the dithiocarbamate ligand centers around its ability to stabilize Ni$^{IV}$ (Fackler, Avdeef & Fischer, 1973), an unusual oxidation state of Ni. The ability of the dithiocarbamate ligand to delocalize positive charge from the metal center is believed to be an important factor in the chemistry of this ligand. In addition to monomeric complexes of dithiocarbamate, dimeric systems have been characterized. Calabro, Harrison, Palmer, Moguel, Rebbert & Burmeister (1981) report the observation of an Au$^{II}$ dithiocarbamate dimer complex upon oxidation of [Au(dtc)]$_2$ with Br$_2$ at low temperatures.

There are three known modifications of bis(diethyl-dithiocarbamato)Ni$^{II}$. The monoclinic α form (Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1965) is the stable modification, while there are two less-stable tetragonal forms, β and γ (Vaciago & Fasana, 1958). In the course of our work extending the chemistry of dtc to trimeric systems we isolated the β form of [Ni{$S_2CN(C_2H_5)_2$}$_2$], [Ni(dtc)$_2$]. In this paper we report the determination of the crystal structure of the β modification of bis(diethyldithiocarbamato)nickel, [Ni{$S_2CN(C_2H_5)_2$}$_2$], obtained from the reaction of an Ni$^{II}$ salt with sodium diethyldithiocarbamate. As judged by the e.s.d.'s of the fractional positional parameters as well as those of the distances and angles, the structure reported here is far more precise than the report by Bonamico *et al.* (1965) (monoclinic; $P2_1/c$, $a = 6 \cdot 189$, $b = 11 \cdot 537$, $c = 11 \cdot 603$ Å, $\beta = 95°51'$, $R = 0 \cdot 101$) for the structure of the α form.

**Experimental.** The complex bis(diethyldithiocarbamato)nickel was obtained from a reaction of sodium diethyldithiocarbamate, Na(dtc), with a nickel octanoate/ethyl borate mixture. The crystals were grown by slow evaporation of the product from a solution of THF/CHCl$_3$/Et$_2$O.

Single multi-faceted green crystal of approximate dimensions 0·25 × 0·20 × 0·25 mm mounted in a random orientation on a glass fiber. Tetragonal symmetry suggested on the basis of interaxial angles and confirmed by a Delaunay reduction. Axial lengths checked by comparison with the interlayer spacings observed in axial photographs. Refined cell parameters obtained from the setting angles of 19 reflections with $10 < 2\theta < 25°$. Data collection carried out at room

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